Lithium-Sulfur Batteries: From Materials Understanding to Device Integration

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Co-PI's: Jun Liu, Jie Xiao (PNNL)

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2018 DOE Vehicle Technologies Program Annual Merit Review
June 18-21, 2017

Project ID: bat361

Overview

Timeline

- Start: Oct 1, 2016
- End: Sep 30, 2021
- Percent complete: 30%

Budget

- Total project funding $50,000k from DOE
- Funding for FY17 $10,000k
- Funding for FY18 $10,000k

Barriers

Barriers of batteries

- High cost (A)
- Low energy density (C)
- Short battery life (E)

Targets: cost-effective and high-energy electrode materials and batteries

Partners

- Collaboration
  - Battery 500 PI's
  - BMR program PI's
  - Prof. Steve Chu, Prof. Bruce Dunn
  - SLAC: In-situ X-ray

BATTERY 500 CONSORTIUM

Project Objective and Relevance

Objective

- Design and fabricate sulfur cathodes with high capacity and stability with long cycle life.

- Design and fabricate Li metal anodes with high capacity, high coulombic efficiency and long cycle life.

- Screen electrolyte and additives for stable anodes and cathodes.

- Develop lithium-sulfur full batteries with 500 Wh/kg specific energy to power electric vehicle and decrease the high cost of batteries.

Milestones for FY17 and 18

Battery 500 Milestones for Li-S Batteries

1) Complete the baseline property of Li-S cathode required to reach 300 Wh/kg based on Battery500 cell design. (Dec-17). **Completed**

2) Complete the set-up of in-situ characterization of full cells. (Mar-18) **Completed.**

3) Provide polymer membranes and Li metal protection methods in coin cells for stage 2 coin cell testing. (Jun-18) **On track.**

4) New polymer membranes and Li metal anode incorporated in pouch cells required to reach 350 Wh/kg cells based on Battery500 cell design. (Sep-18) **On track.**

BATTERY 500 CONSORTIUM

Approach/Strategy

Cell design, fabrication and validation

1) Establish cell parameters and requirements for coin cells and pouch cells
2) Integrate nanostructured materials in full cells

Nanostructured sulfur cathodes design and synthesis

1) Develop novel sulfur nanostructures with multi-functional coatings for the confinement of sulfur/lithium polysulfides to address the issues of active materials loss and low conductivity.
2) Develop/discover optimal nanostructured materials that can capture the polysulfide dissolved in the electrolyte.

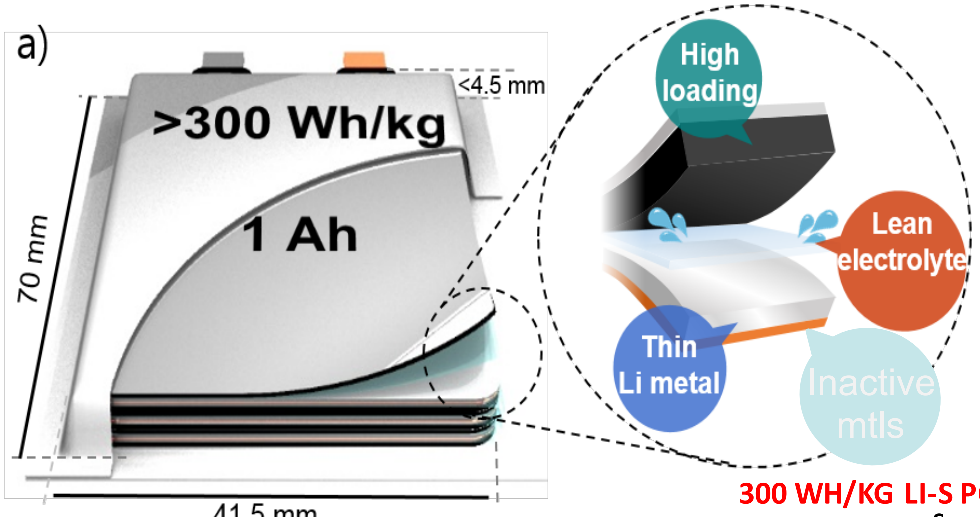
3D Li metal host anode and interfacial modification

1) Design and synthesize Li metal with 3D host composite to overcome volume expansion and contraction problems.
2) Design surface modification techniques to generate stable interphase by gas phase reaction and advanced polymer coatings
3) Screen electrolytes which can generate stable interface.

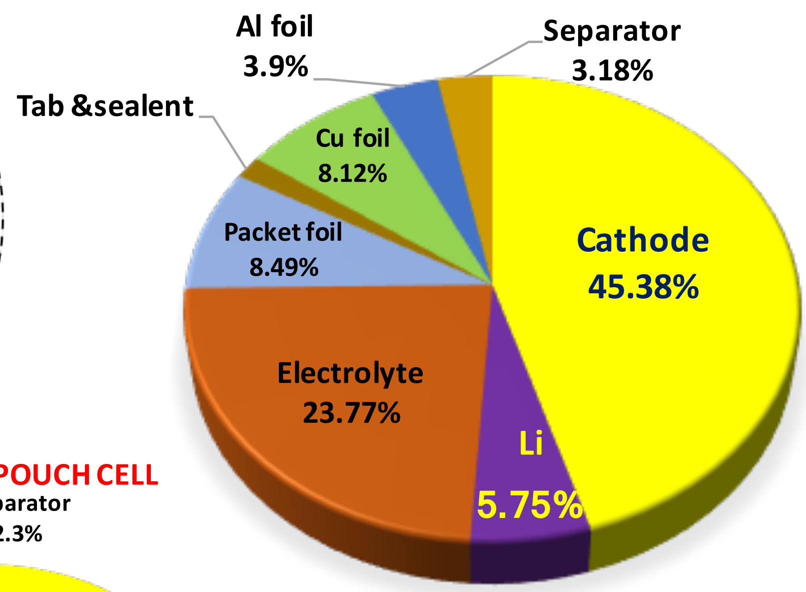
Structure and property characterization

1) Transmission electron microscopy
2) Cryogenic electron microscopy
3) In operando X-ray diffraction and transmission X-ray microscopy

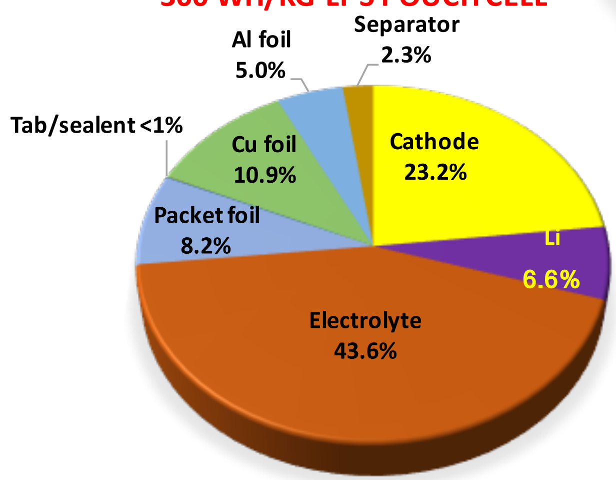
Cell level problems for > 300 Wh/kg Li/NMC and Li/S Cells



300 WH/KG LI/NMC POUCH CELL



300 WH/KG LI-S POUCH CELL



Accomplishment

Battery500 Testing Requirements and Protocols for Li-S Cells

FY18 Coin Cell Testing Protocol for Li/S (for FY18 350 Wh/kg milestone)

1. **Sulfur Cathode requirements:**
   a. Minimum areal capacity: 6 mAh/cm^2

2. **Coin cell assembly:**
   a. CR2032 coin cell kits
   b. Sulfur cathode disk, 1 piece
   c. PE separator, 20 μm thick, ¾" diameter, 1 piece
   d. Baseline electrolyte: 1M LiTFSI-DOL/DME(1:1) +2% $LiNO_3$
   d1. Electrolyte amount: excessive amount of electrolyte can be used for initial evaluation of sulfur cathode
   d2. Final testing/results comparison needs to use lean electrolyte with electrolyte/capacity ratio = 3 g/Ah
   e. Li metal foil: 1.56 cm diameter (1 piece)
   e1. Initial testing can use thick Li metal foil e.g.250 μm Li from MTI
   e2. Final testing/results comparison needs to use thin Li foil (and lean electrolyte as described in d2) with N/P =1.6 (similar as in the pouch cell), e.g. ca.50 um Li (on Cu foil).
   f. SS spacer (1 piece) and SS spring (1 piece)
   g. Crimp at 1000 psi (MTI manual crimper)

3. **Testing protocols:**
   a. Testing temperature: 25°C
   b. Voltage range: 1.8 -2.6 V
   c. Resting time: 8 hrs
   d. Formation process: 2 cycles at C/20 rate (0.3 mA/cm^2) for charge and discharge; No rest between charge and discharge.
   e. Subsequent cycling procedure depends on your own need. Constant voltage (CV) mode is NOT needed at the end of charge to avoid shuttle reactions.

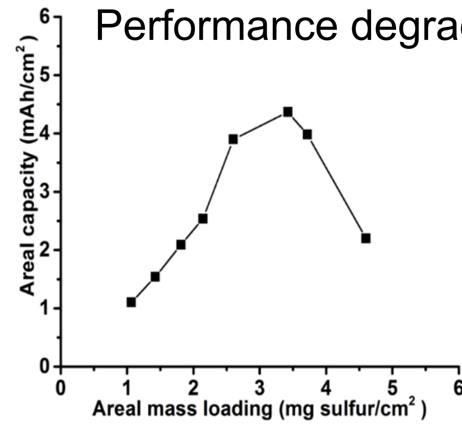
BATTERY500 CONSORTIUM

Accomplishment

Electrode Materials Design for Li-S Batteries

- Develop nanostructured electrodes for encapsulation and high S loading;
- Understand the effect of interfacial binding;
- Understand the fundamental reaction mechanisms;
- Cell level integration and optimization for high S loading and lean electrolytes

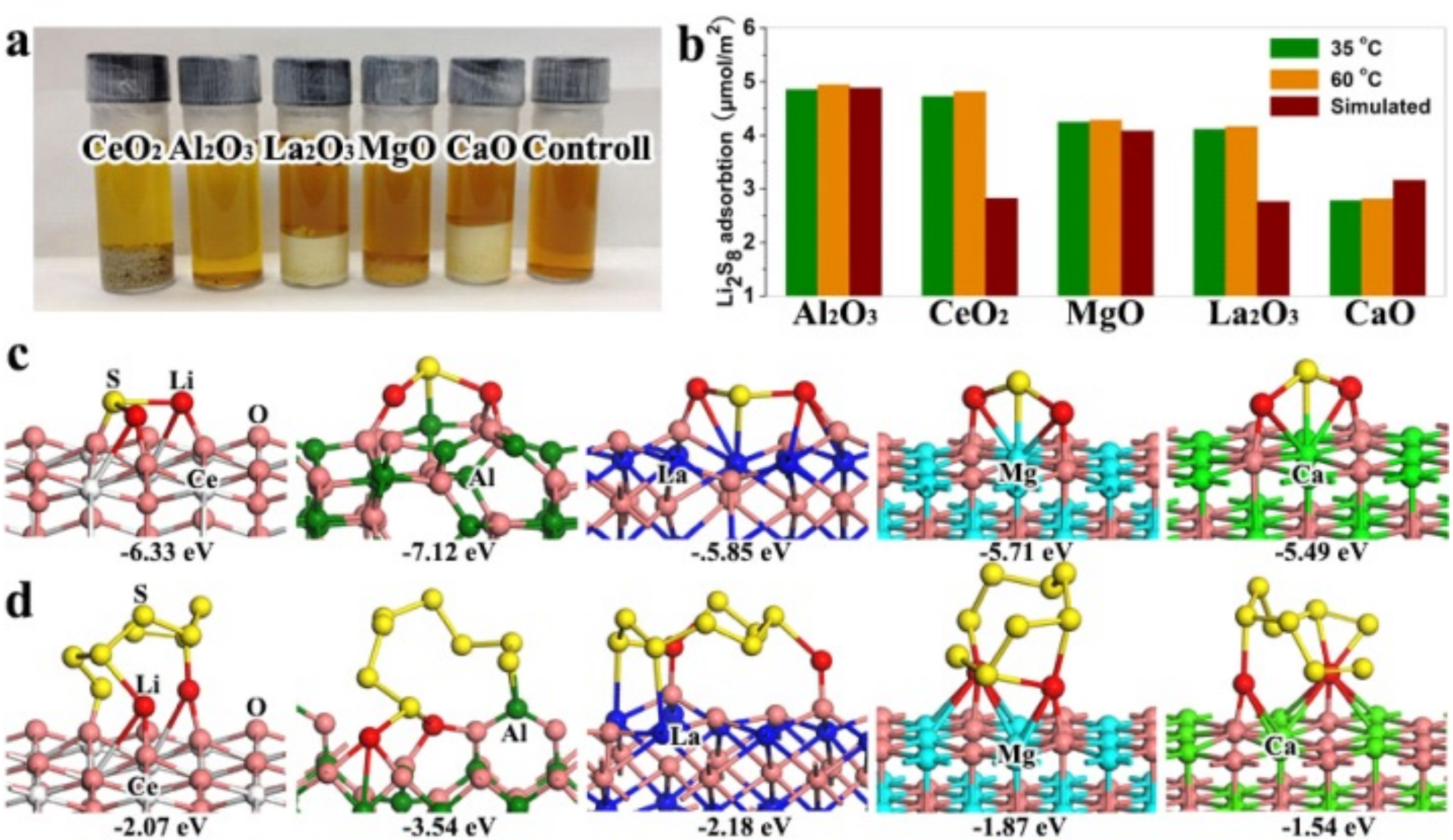
Performance degrades with high S



D. Lv et al., Adv. Energy Mater. Adv. Energy Mater. ***2015,*** *1402290*

Accomplishment

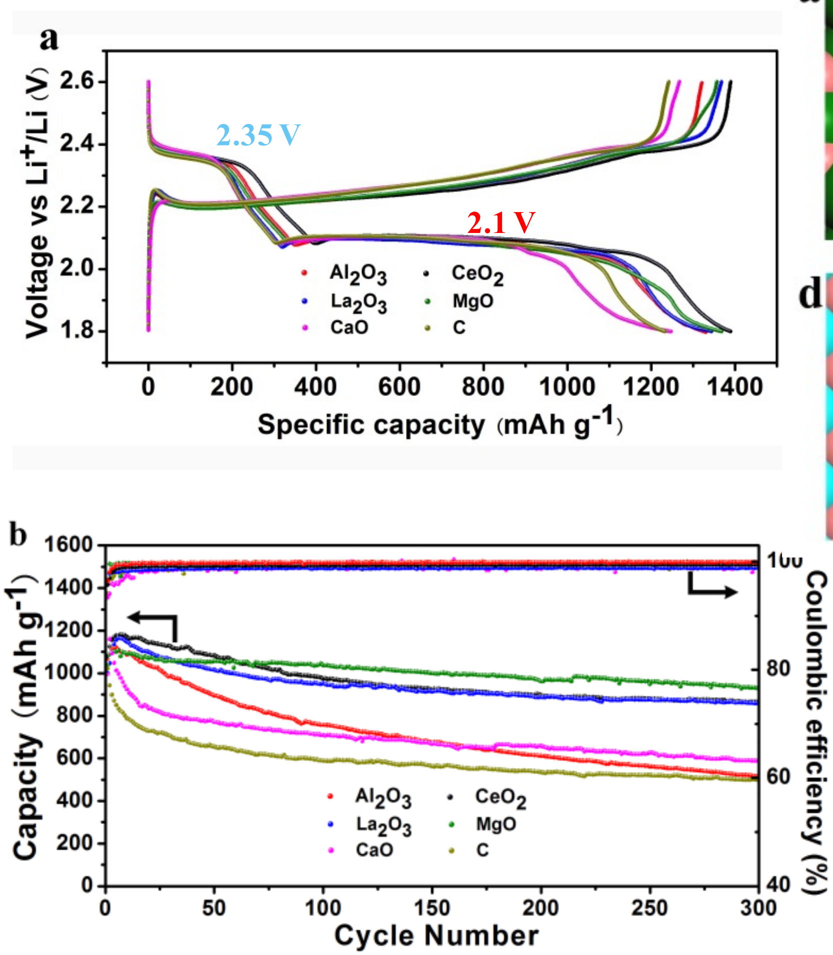
Polysulfide capture on the surface of metal oxides is monolayered chemisorption confirmed by combined experiment-DFT computations

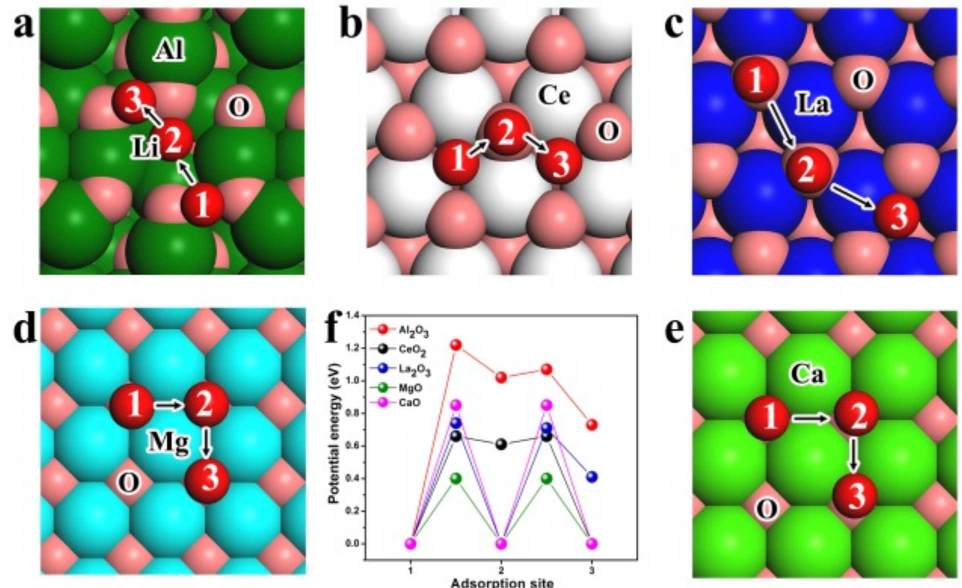


Cui et. al
Nature Communications, 7, 11203 (2016)

Accomplishment

Oxide selection criterion: balance optimization between sulphides adsorption and diffusion on the metal oxides surface





➢ Lithium sulphide species can strongly adsorb, however, difficult to diffuse on Al_2O_3

➢MgO with suitable adsorption energies of lithium sulphur species and small diffusion barriers of Li

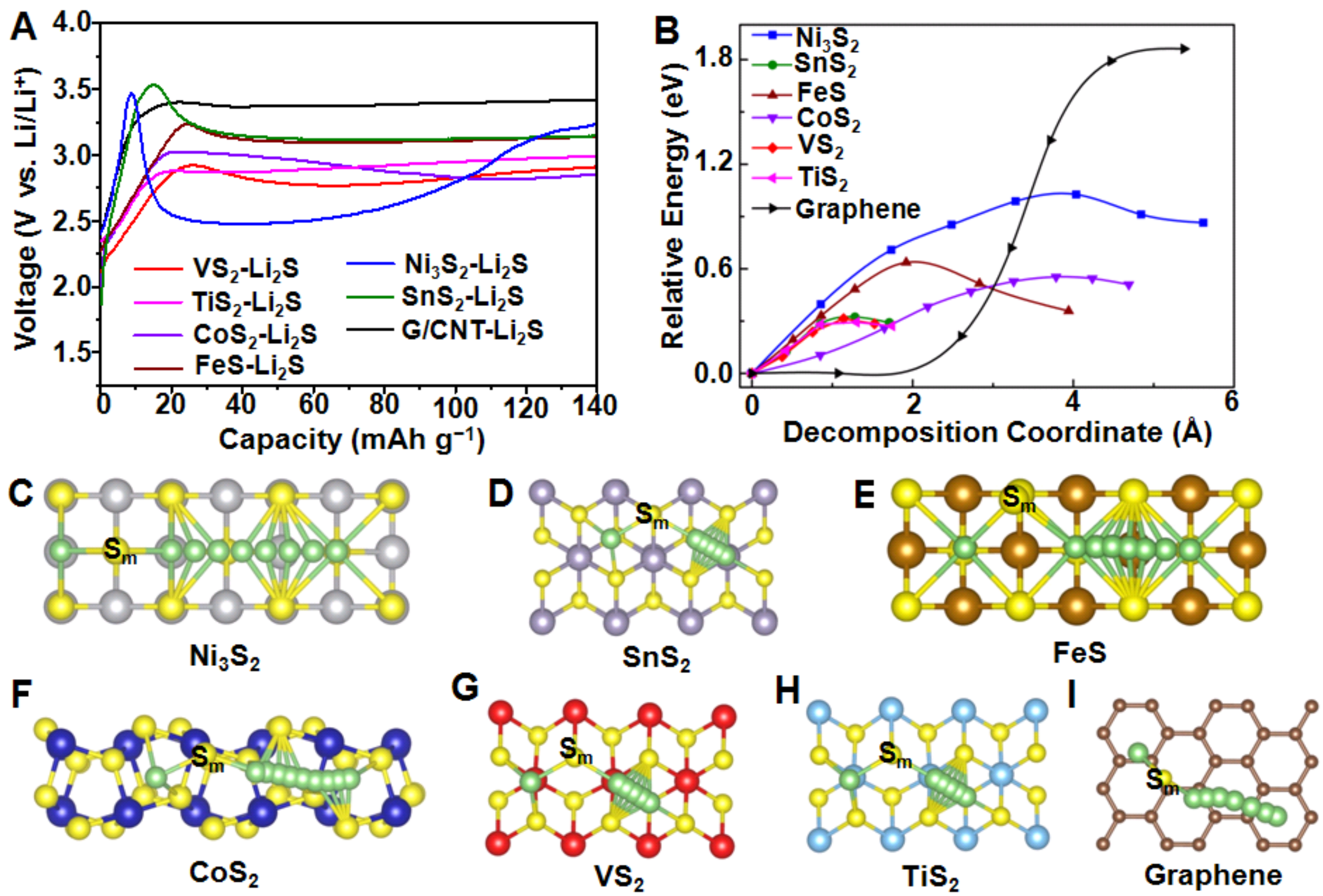
➢CeO_2(111) and La_2O_3(001) surfaces with similar diffusion barrier of 0.66 eV have the similar cycling performance.

Cui et. al
Nature Communications, 7, 11203 (2016)

Accomplishment

Catalytic effects of substrate: decomposing barriers for Li_2S

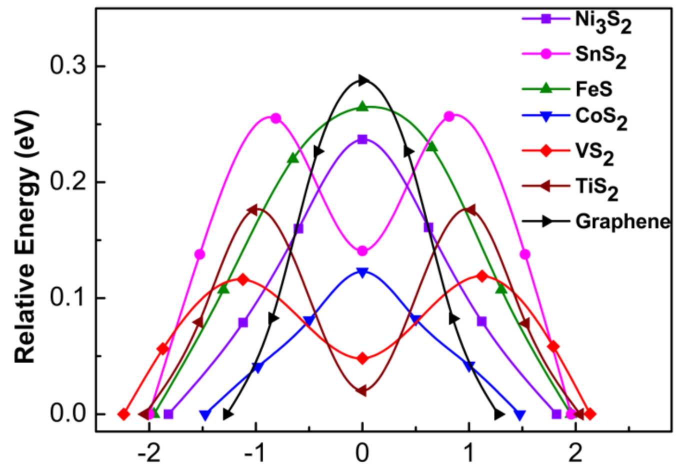
$$Li_2S \rightarrow LiS + Li^+ + e^-$$

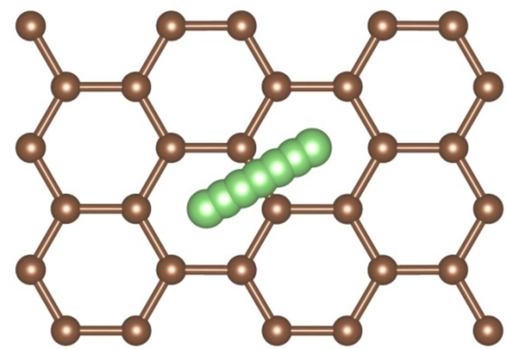


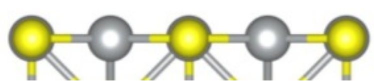
Cui group, PNAS, 114, 840 (2017)

Accomplishment

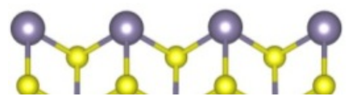
Lithium ion diffusion properties and mechanism



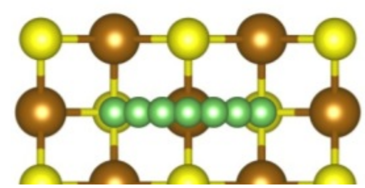




Ni_3S_2

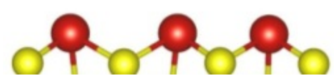


SnS_2



FeS

CoS_2



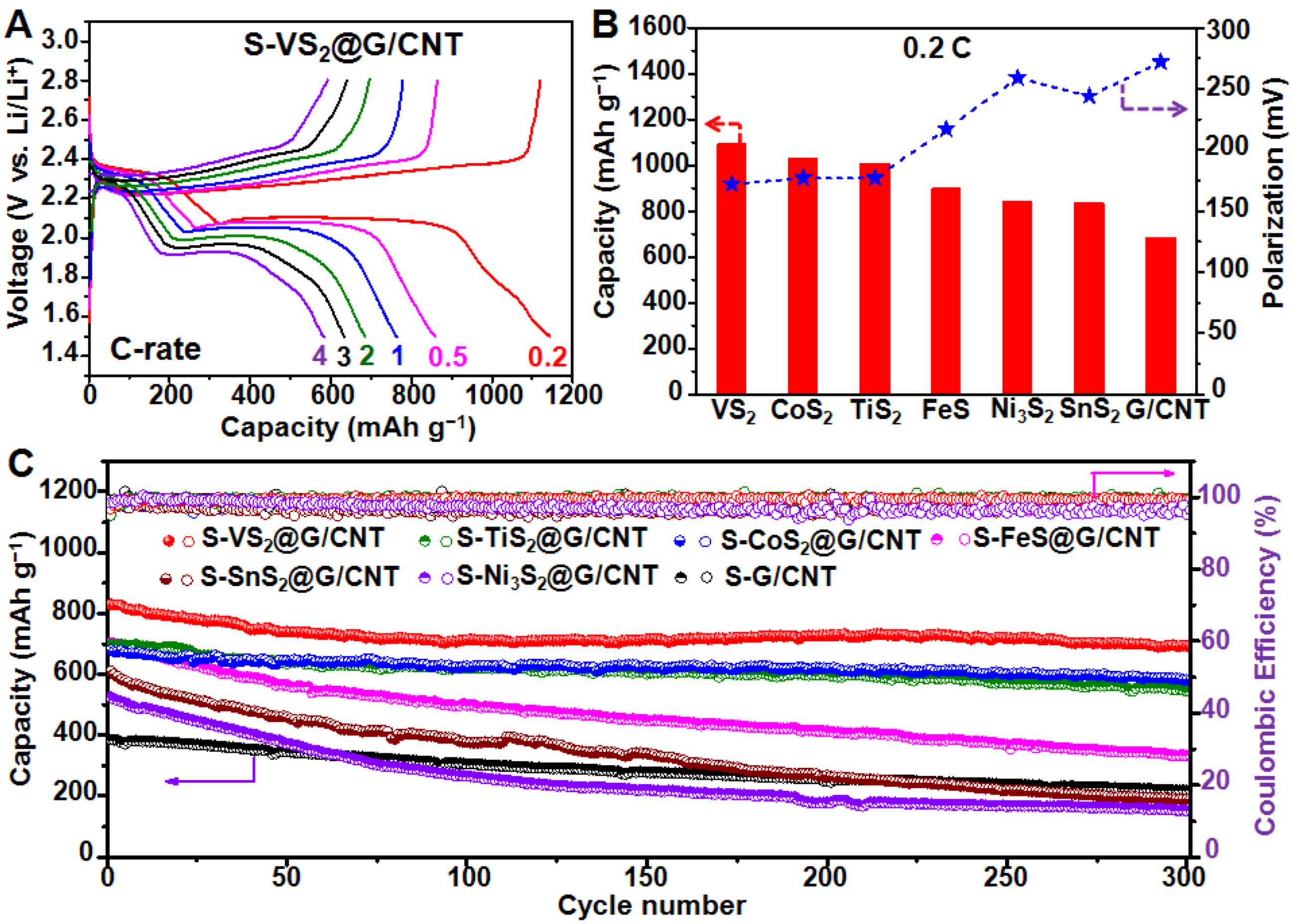
VS_2

TiS_2

Cui group, PNAS, 114, 840 (2017)

Accomplishment

Electrochemical performance

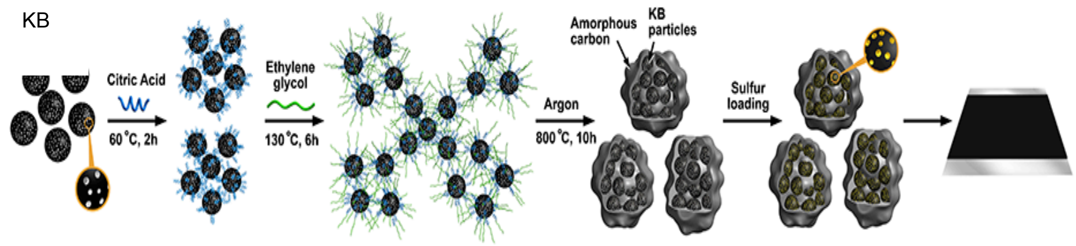


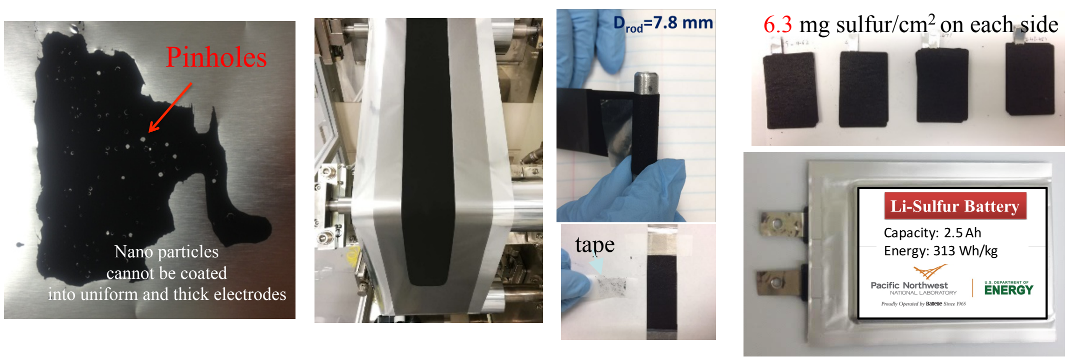
BATTERY 500 CONSORTIUM

Cui group, PNAS, 114, 840 (2017)

Accomplishment

Li-S Pouch Cells: From Materials Synthesis to Pouch Cell Preparation Using Scalable Materials and Processes



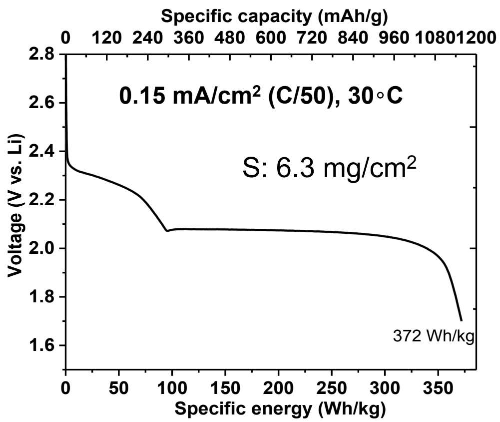


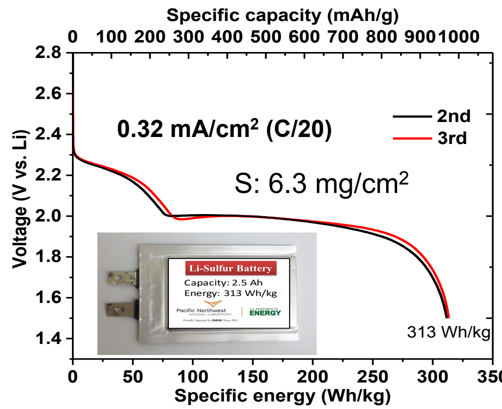
- All S/C materials are synthesized at PNNL (U.S. Patent No. 9,577,250).
- Adjustable S loading (2-10 mg/cm^2) with uniform coating is demonstrated.
- Suitable for continuous coating process with consistent quality.

D. Lv et al., Adv. Energy Mater. ***2015,*** *1402290*

Accomplishment

Identified Key Challenges in Li-S Pouch Cells

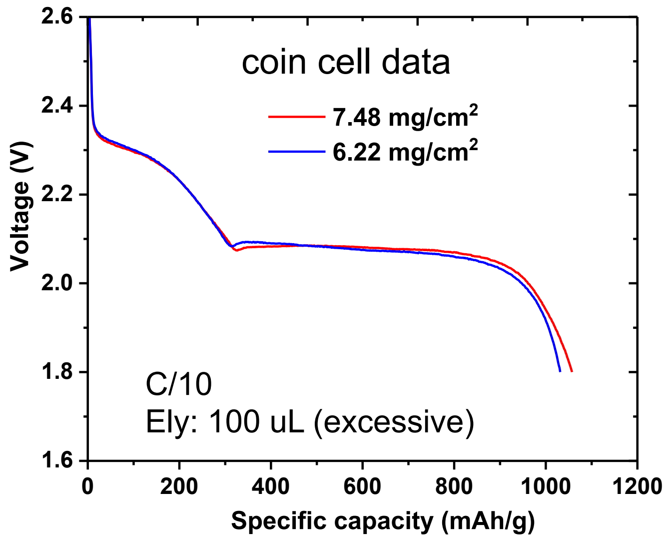


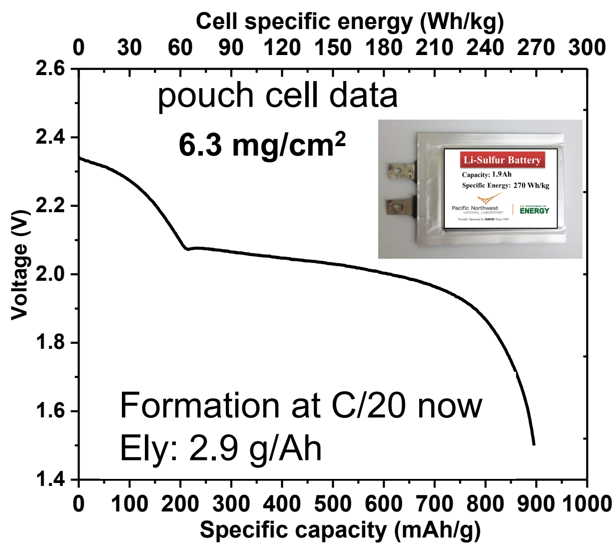


- Highly porous S/C electrodes is very difficult to be fully wetted.
  - Slow rate (C/50) and 30°C do help wetting and thus high utilization of S (1156 mAh/g)
- Poor rate capability:
  - C/20: specific capacity decreases to 980 mAh/g; cell energy reduces to 313 Wh/kg
- Cycling is challenging for greater than 10 cycles due to deep stripping/ deposition of Li (6.3 mAh/cm^2 without considering side reactions).

Accomplishment

Li-S: From Coin Cells to Pouch Cells





- ❖ Coin cell: high sulfur loading electrodes fully release the capacity.
- ❖ Pouch cell: Multilayer stacking/pressing and lean electrolyte brings more challenges than in Li/NMC cells.
- ❖ Solutions: rest for longer time and formation cycle at 30◦C
- ❖ Still under test….

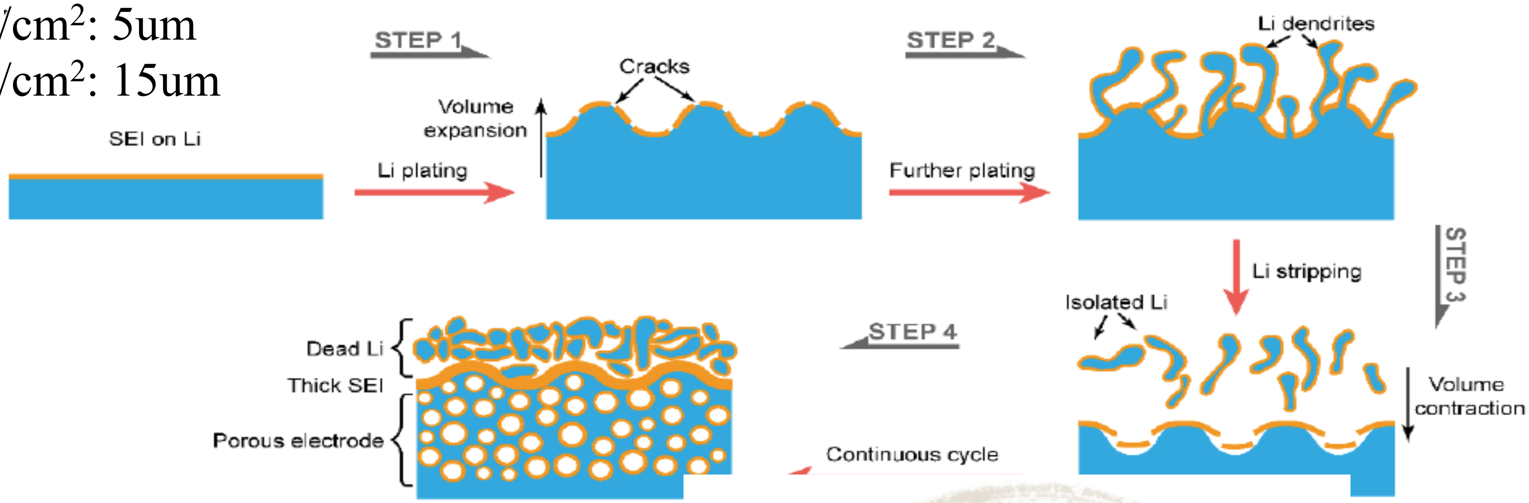
BATTERY 500 CONSORTIUM

Jie Xiao

Jun Liu

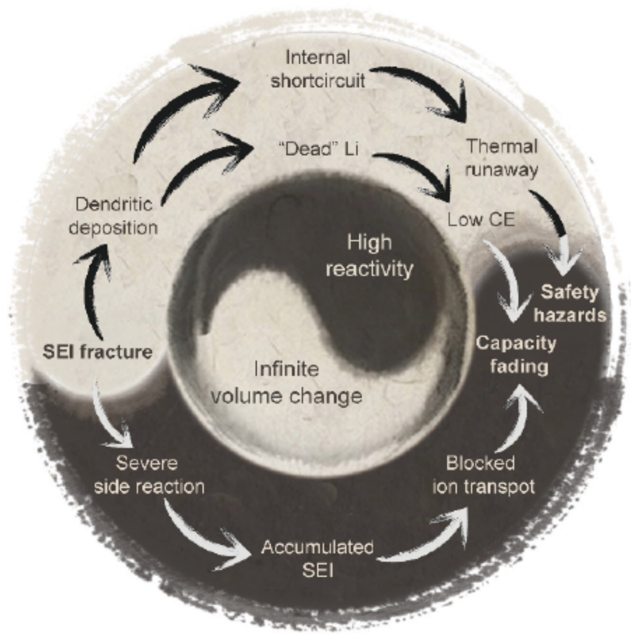
Accomplishment: Addressing Li metal challenge

1 mAh/cm^2: 5um
3 mAh/cm^2: 15um



Root causes:

- High reactivity
- Infinite volume change



D. Lin, Y. Liu, Y. Cui
Nature Nanotech. **12**, 194 (2017).

Accomplishment

- **Stable "Host" design**

Nature Nanotech. **11**, 626 (2016)

Nature Commun. **7**, 10992 (2016)

Nature Energy **1**, 16010 (2016)

PNAS **113**, 2862 (2016)

Nano Lett. **17**, 3731 (2017)

PNAS **114**, 18 4613 (2017)

Sci. Adv. **3(9),** e1701301 (2017)

- **Interfacial Engineering**

Nature Nanotech. **9**, 618 (2014).

Nano Lett. **14**, 6016 (2014).

Nature Commun. **6**, 7436 (2015)

ACS Energy Lett. **1**, 1247 (2016)

J. Am. Chem. Soc. **139**, 4815 (2017)

J. Am. Chem. Soc. **139**, 11550 (2017)

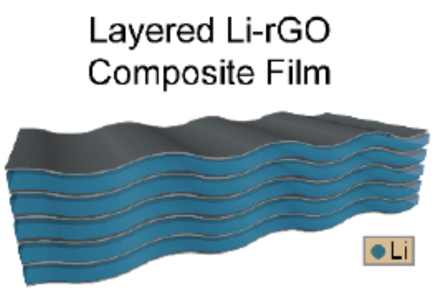
Sci. Adv. **3**, eaao3170 (2017)

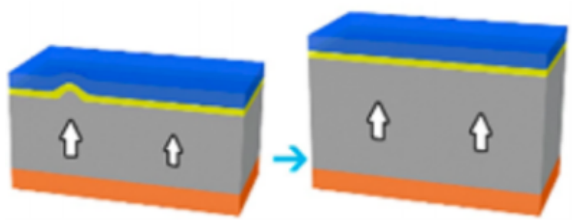
- **Materials characterizations**

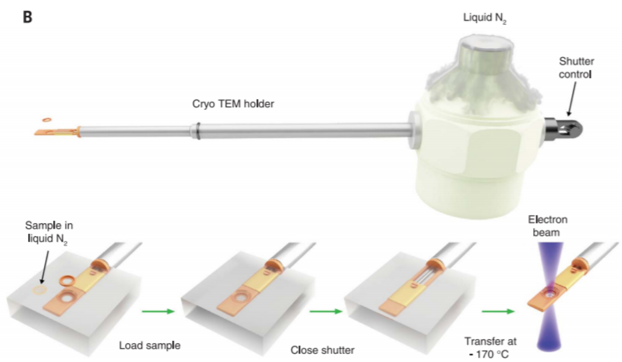
Science **358**, 506 (2017)

PNAS, **114**, 12138 (2017)

Nano Lett. **17**, 5171 (2017)

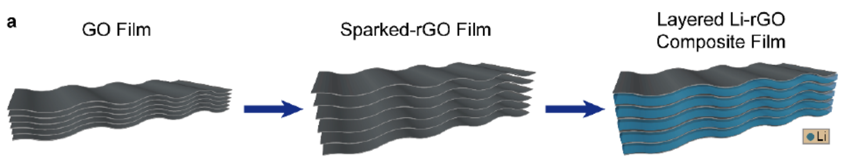






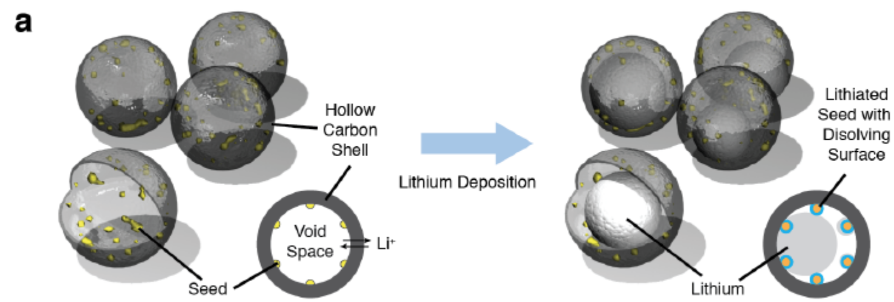
Accomplishment: Previous Host Design

Layered Li-rGO composite anode



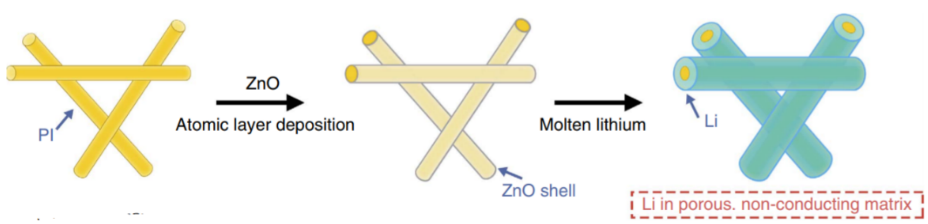
Nature Nanotech. **11**, 626 (2016)

Seeded nanocapsules for Li metal



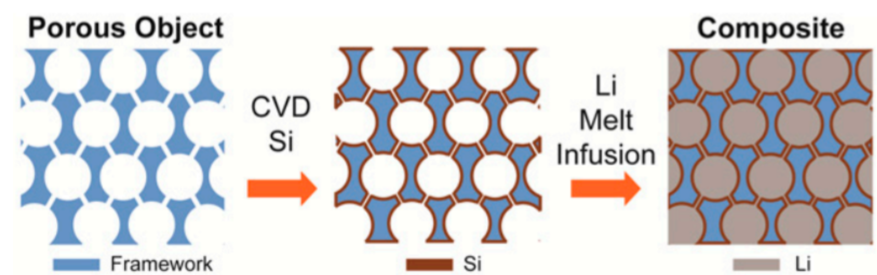
Nature Energy **1**, 16010 (2016)

ALD ZnO lithiophilic polymeric scaffold



Nature Commun. **7**, 10992 (2016)

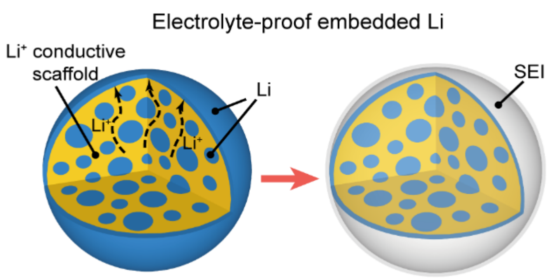
CVD Si lithiophilic scaffold

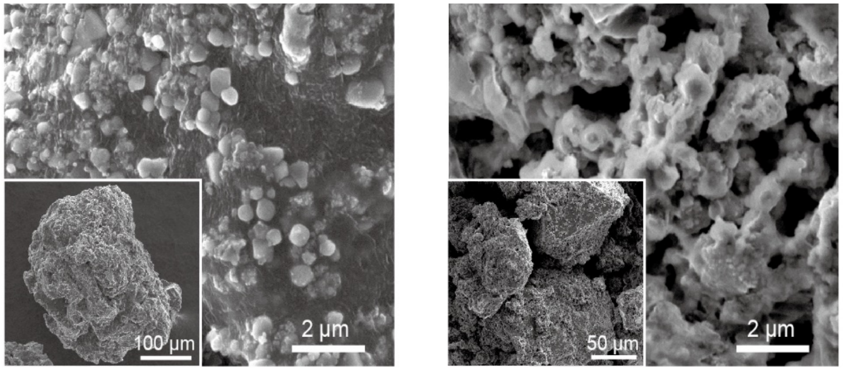


PNAS **113**, 2862 (2016)

Accomplishment

Stable Host for Li metal: Li-SiO composite

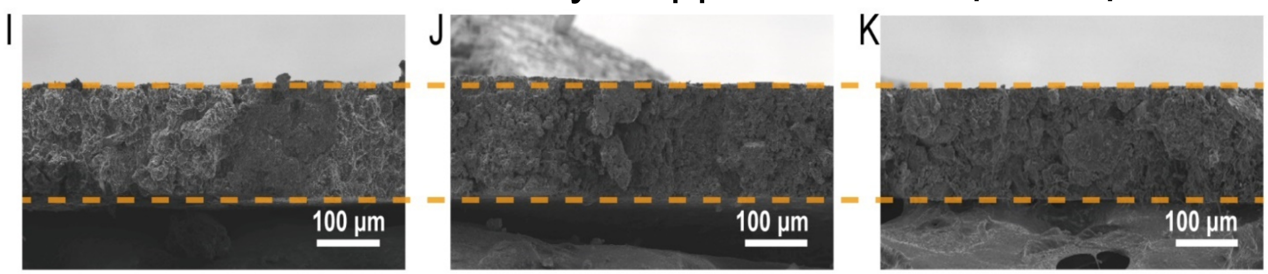




$$SiO + m\,Li \xrightarrow{>300\ ^\circ C} \underbrace{Li_xSi + Li_2O}_{Li^+\ \text{conductive scaffold}} + (m\text{-}x\text{-}2)\ Li$$

Extra Li embedded in the scaffold

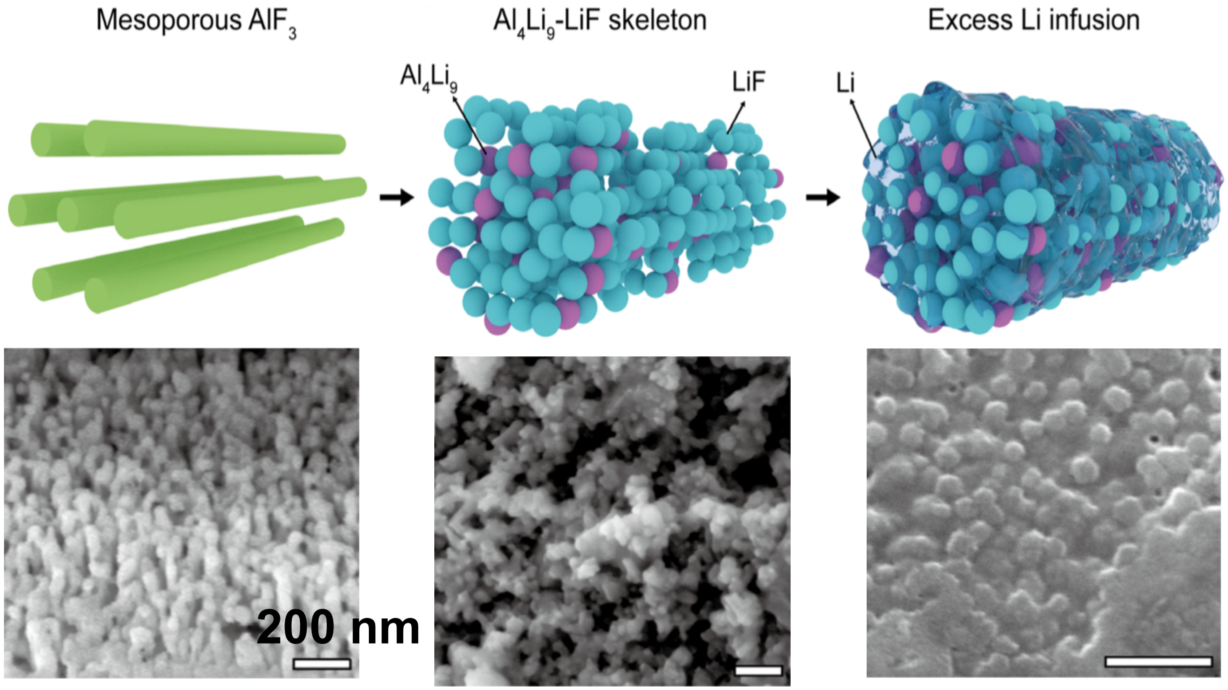
Pristine | Fully stripped | Strip and plate back



D. Lin, Y. Cui *et al.*
PNAS **114(18)**, 4613 (2017) .

Accomplishment

Stable Host for Li metal: Li-AlF_3 composite



$$AlF_3 + m\ Li \xrightarrow{>300\ °C} \underbrace{Li_xAl + LiF}_{Li^+\ \text{conductive scaffold}} + (m-x-1)\ Li$$

Li⁺ conductive scaffold   Extra Li embedded in the scaffold

H. Wang, D. Lin, Y. Cui, *et al.* *Sci. Adv.* **3(9),** e1701301 (2017)

Accomplishment

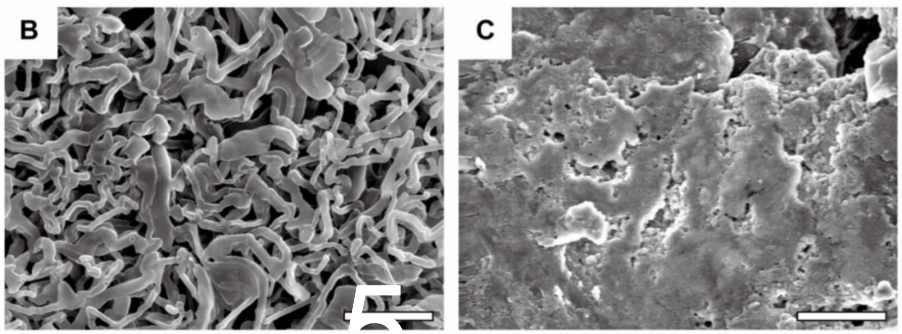
Stable Host for Li metal: Li-AlF_3 composite

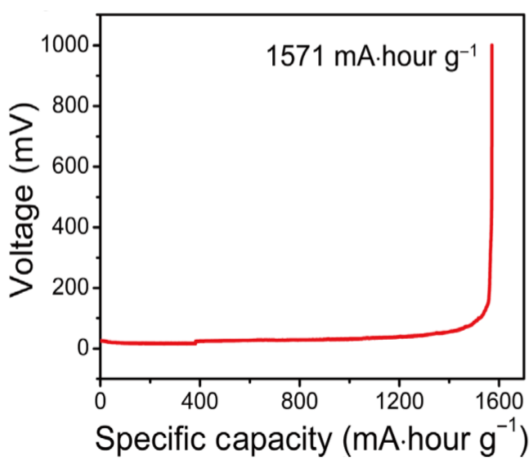
Li foil

Composite anode

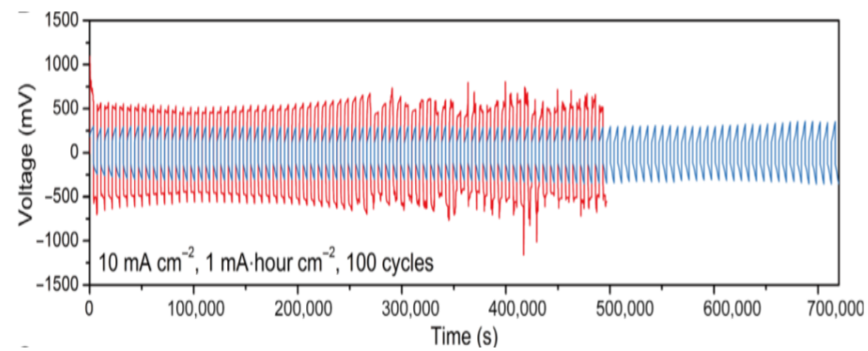
- Large current density
- Zero volume change

1 mA cm^{-2}, 1 hour

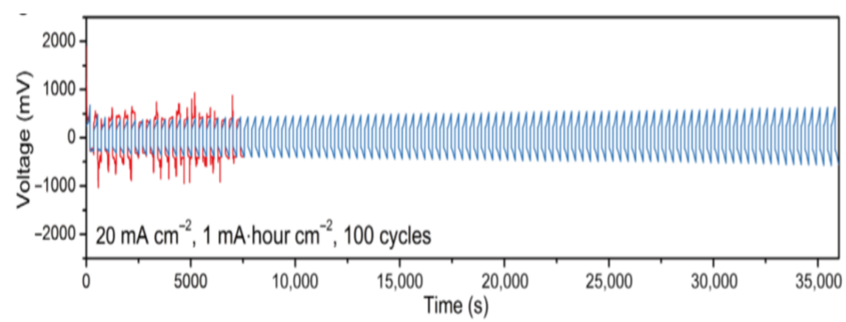




10 mA cm^{-2}

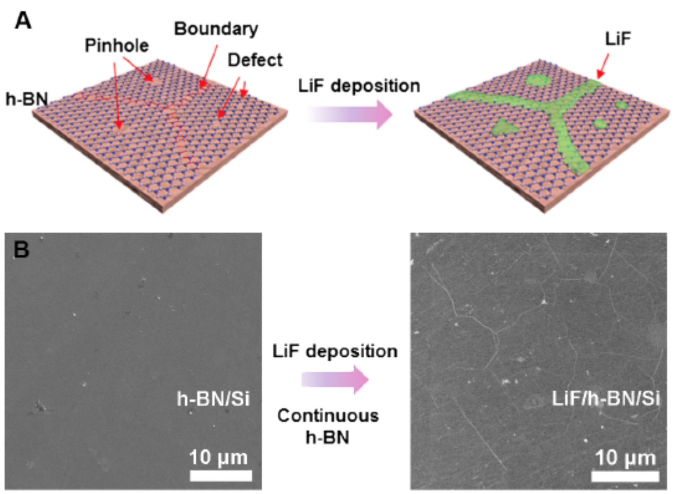


20 mA cm^{-2}



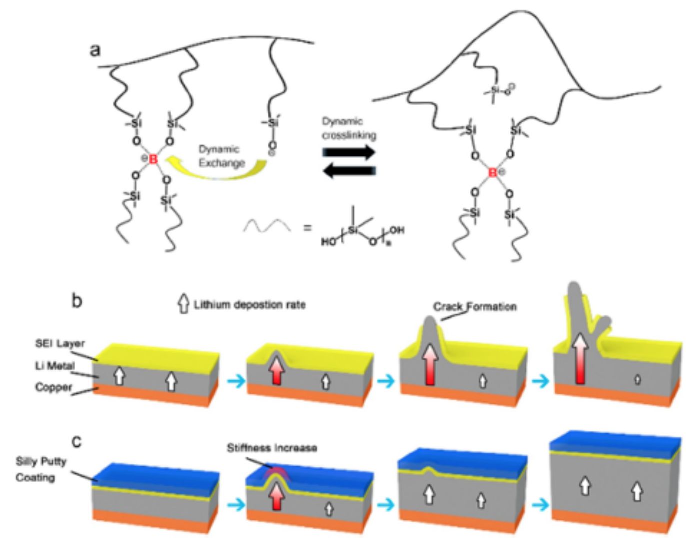
Accomplishment

Stitching h-BN by atomic layer deposition of LiF as a stable interface for lithium metal anode



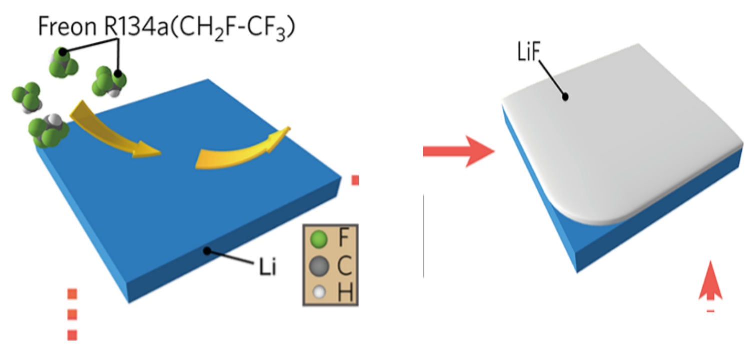
Jin Xie, Y. Cui *et al*. *Science Advances* (2017).

Lithium Metal Anodes with an Adaptive "Solid-Liquid" Interfacial Protective Layer



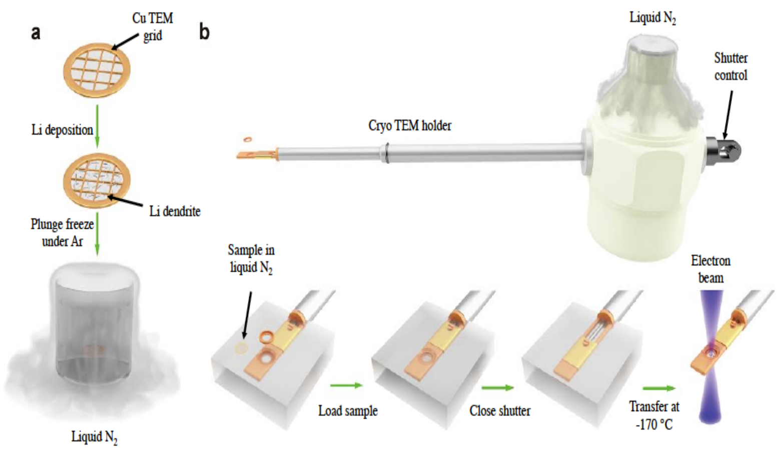
Kai Liu, Allen Pei, Z. Bao, Y. Cui *JACS* (2017).

LiF coating



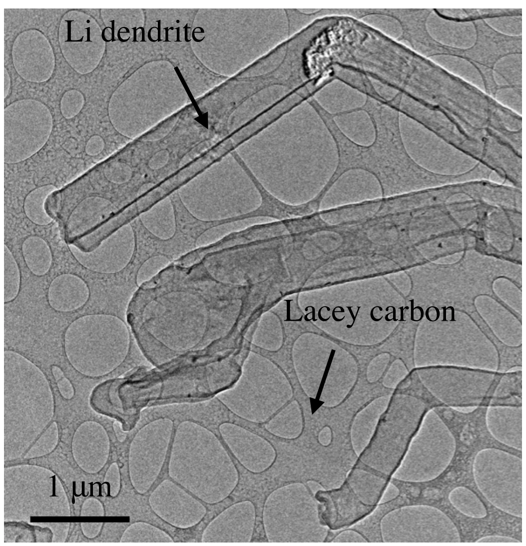
D. Lin, B. Dunn, Y. Cui, *et al.* *Nano Lett.* **17**, 3731 (2017)

Accomplishment

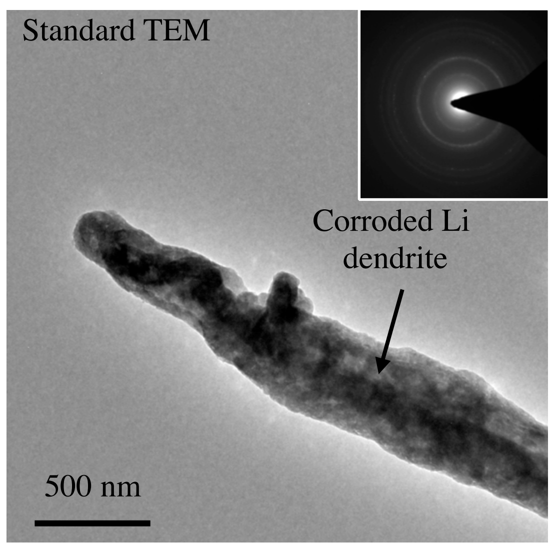


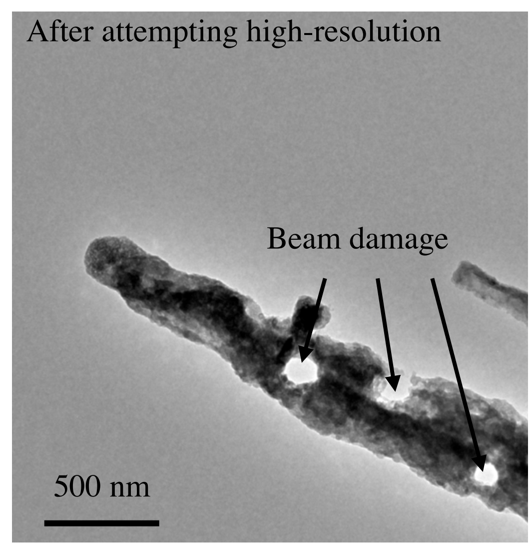
Cryo-EM for Battery Materials

Cryo-EM



Standard TEM 1s air exposure

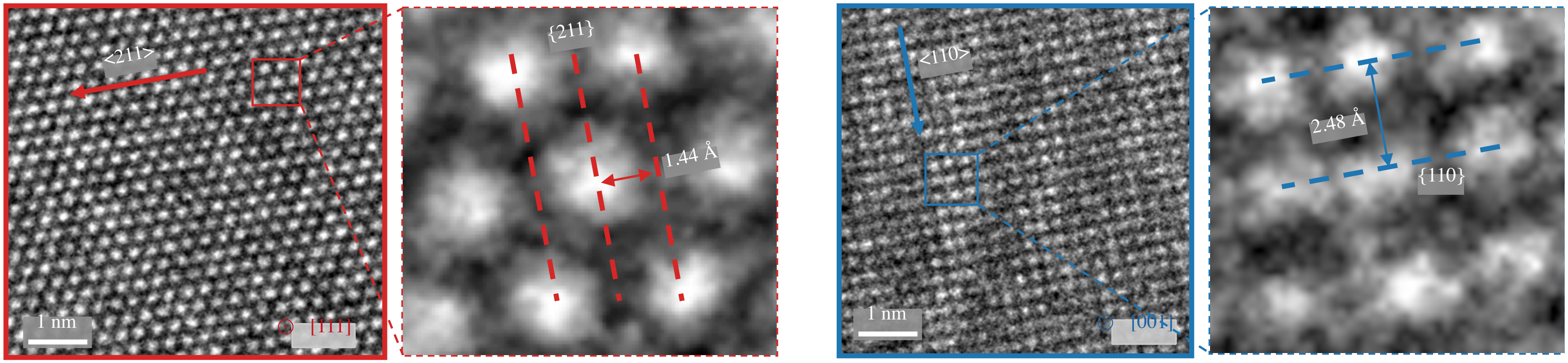




Yuzhang Li, Yanbin Li, Steven Chu, Yi Cui et. al. *Science* 358, 506, 2017.

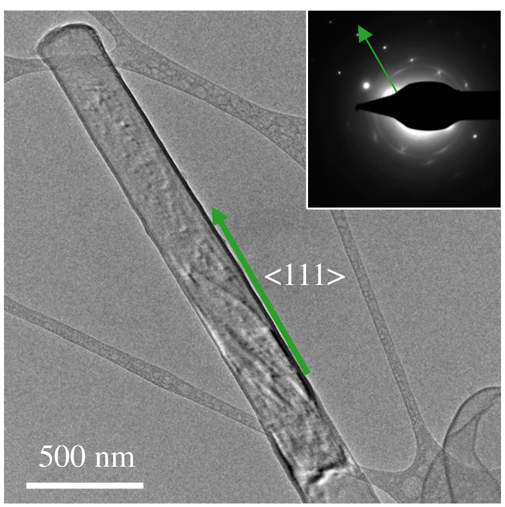
Accomplishment

Individual Li metal atoms can be resolved by Cryo-EM

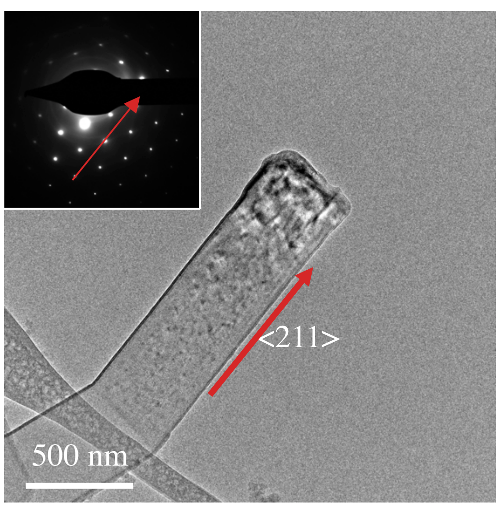


Three growth directions are observed

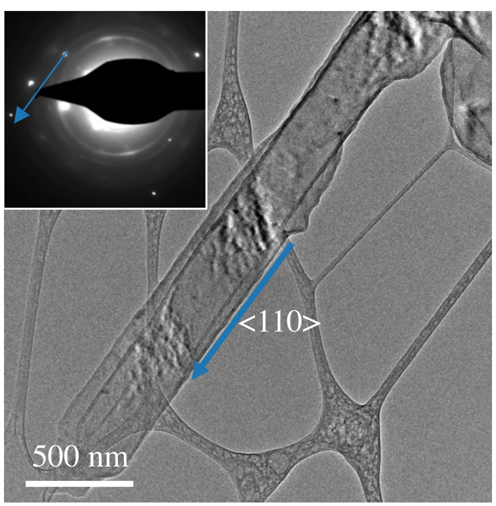
<111> (49%)



<211> (32%)



<110> (19%)



Yuzhang Li, Yanbin Li, Steven Chu, Yi Cui et. al. *Science* 358, 506, 2017.

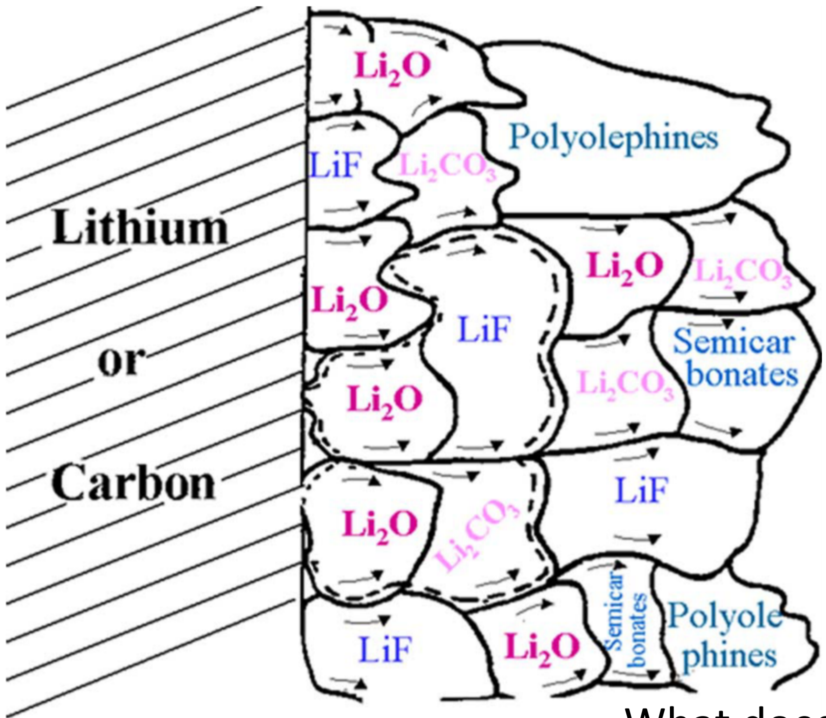
SEI structure is not fully understood

SEI species include:

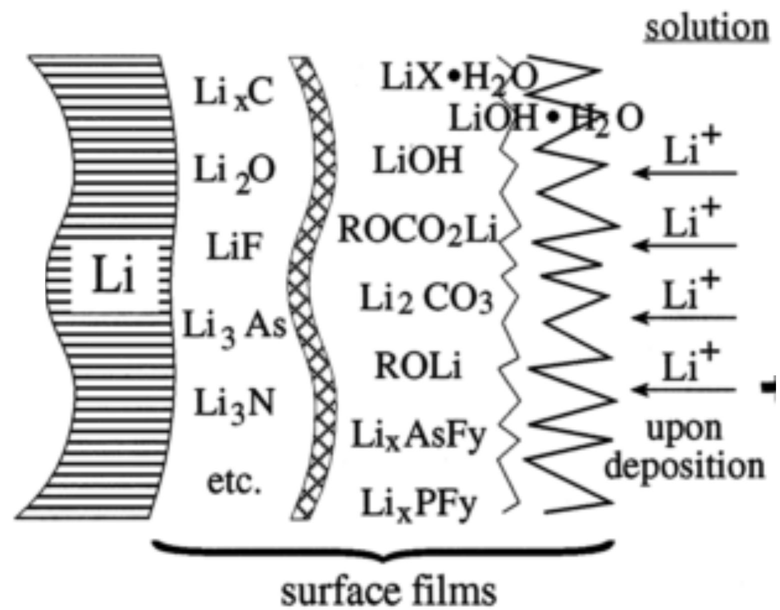
Inorganics - Li_2O, Li_2CO_3, Li_3N, LiF, LiOH,

Organics - ROLi, RCOOLi, ROCOLi, $RCOO_2Li$, $ROCO_2Li$

Mosaic Model



Layered Model



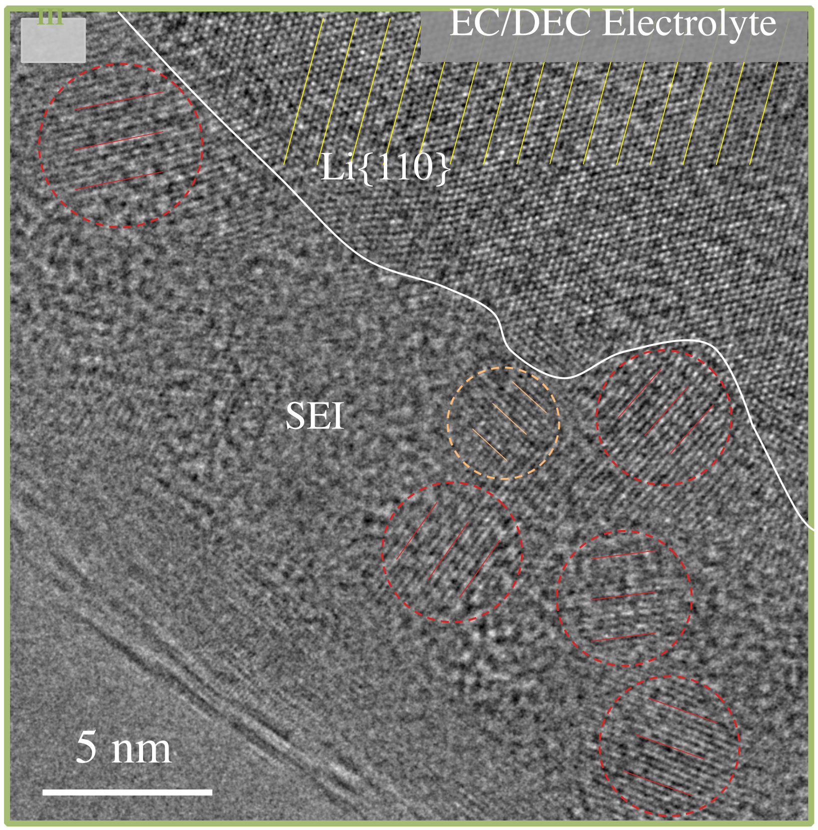
What does SEI look like?

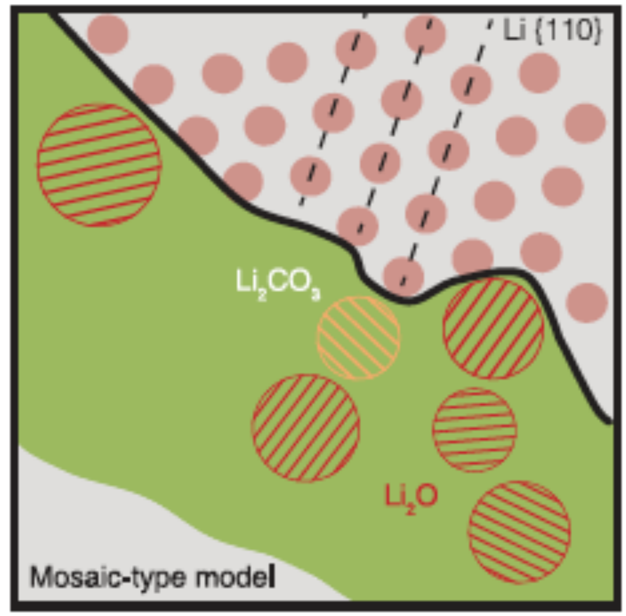
What makes a SEI "good"?

Peled, E. *J. Electrochem. Soc.* **144,** L208 (1997).
Aurbach, D., Moshkovich, M., Cohen, Y. & Schechter, A.. *Langmuir* **15,** 2947–2960 (1999).
Aurbach, D. *J. Power Sources* **89,** 206–218 (2000).
Pinson, M. B. & Bazant, M. Z. *J. Electrochem. Soc.* **160,** A243–A250 (2012).

Accomplishment

Our Proposed New SEI Model 1:
Matrix Model

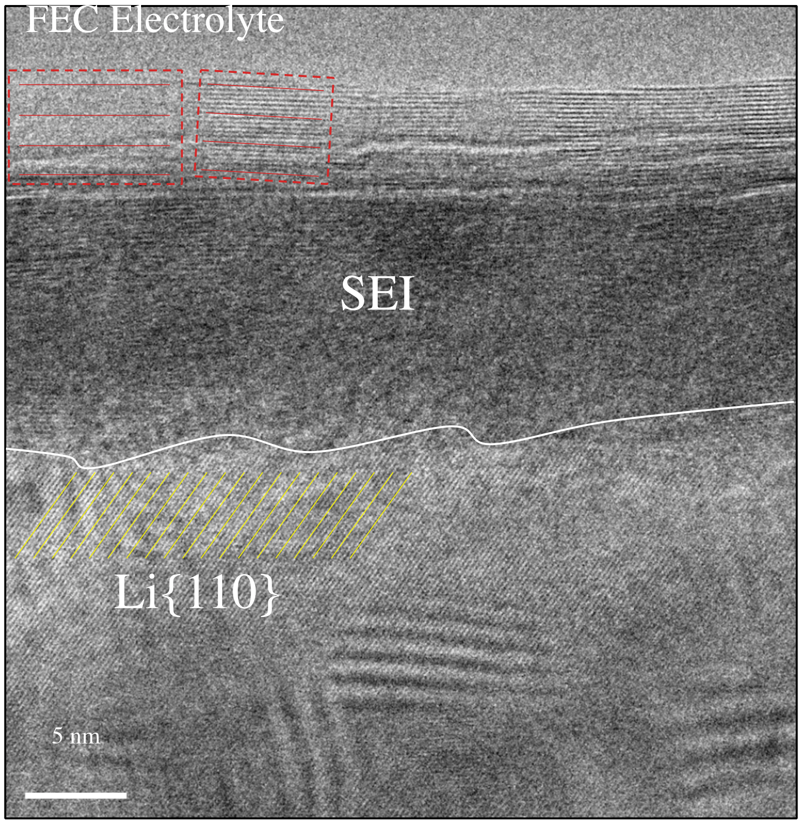


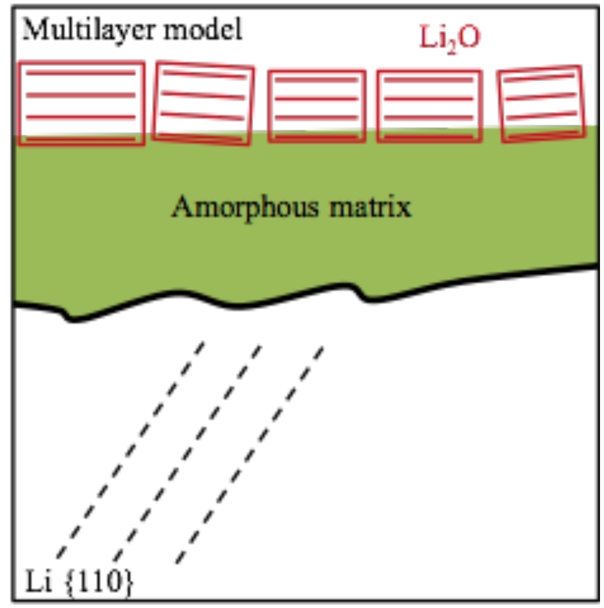


Yuzhang Li, Yanbin Li, Steven Chu, Yi Cui et. al. *Science* 358, 506, 2017.

Accomplishment

Our Proposed New SEI Model 2:
"Inverse" Multilayer Model





Yuzhang Li, Yanbin Li, Steven Chu, Yi Cui et. al. *Science* 358, 506, 2017.

Responses to Previous Year Reviewers' Comments

None.

Collaboration and Coordination

Battery 500 PI's: Jie Xiao, Jun Liu
BMR PI's

SLAC/ Stanford University:
Prof. Zhenan Bao
Prof. Mike Toney
Prof. William Chueh
Prof. Reiner Dauskardt
Prof. Steven Chu

Prof. Bruce Dunn, UCLA

Remaining Challenges and Barriers

- It is difficult to maintain high capacity and excellent cycling stability of lithium-sulfur batteries while increasing the mass loading of active sulfur in the cathode.

- It is challenging to generate Li metal with high coulombic efficiency and long cycle life.

- The cycling of full Li-S batteries is still challenging.

Summary

- **Objective and Relevance:** The goal of this project is to develop stable and high capacity Li metal anodes, sulfur cathodes and the full battery cells to enable high energy lithium-sulfur batteries to power electric vehicles, highly relevant to the VT Program goal.
- **Approach/Strategy:** This project combines advanced nanomaterials design, synthesis, characterization, battery assembly and testing, and guided by theoretical calculations, which have been demonstrated to be highly effective.
- **Technical Accomplishments and Progress:** This project has produced many significant results, meeting milestones. They include identifying the key issues in lithium-sulfur batteries, using rational materials design, synthesis, characterization and simulation. The results have been published in top peer-reviewed scientific journals. The PI has received numerous invitations to speak in national and international conferences.
- **Collaborations and Coordination:** The PI has established a number of highly effective collaborations.
- **Proposed Future Work:** Rational future plan has been designed.

Proposed Future Work

- To understand the interaction between sulfur species and multifunctional binders, and select the optimal materials to re-capture the active sulfur species diffused in the electrolyte.
- To test sulfur cathodes with high areal mass loading at high current densities.
- To further develop approaches for 3D Li metal anodes with stable interfacial modification.
- To develop electrolytes for stable full Li-S battery cells.